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Title of the Invention:

Anti-fogging glass and process for preparing the same

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SPECIFICATION

1. Title of the Invention

Anti-fogging glass and process for preparing the same

2. Claims

(1) An anti-fogging glass, characterized in that a film of an inorganic oxide such as silica and titania having a certain thickness and fine irregularities on its surface is formed on the surface of glass.

(2) A process for preparing an anti-fogging glass, characterized in that a film of an inorganic oxide such as silica and titania is formed in a certain thickness on the surface of glass by sputtering, and the surface of said film is then etched chemically with an etching agent such as hydrofluoric acid under a certain condition.

3. Detailed Description of the Invention

Technical Field

The present invention relates to an anti-fogging glass used in cars and the other vehicles, and to a process for preparing it.

Prior Art

In rainy weather or in the winter season, window glasses and mirror glasses used for cars and the other vehicles are clouded with raindrops or water droplets formed from moistures released from persons in the car, which may result in the lowering of visibility of drivers and thus prevent their driving operation. There have been used the methods for avoiding such cloudiness of window glass and mirror glass by spraying or coating the glasses, for example, with a hydrophilic surface active agent.

Problems to be solved by the Invention

Anti-fogging products using such methods however have the defects of poor durability and the anti-fogging

effect maintaining for only a limited time. In addition, there has been used a method for preventing the cloudiness of glass by sticking for example a transparent plastic sheet comprising a cellulose ester having a hydrophilic group on window glass and mirror glass. However, such a sheet is soft and thus inferior in resistance to scuffing, so that it is difficult to use the sheet for the window glass and mirror glass of cars.

The present invention is intended to solve the problems of the prior art, and the object of the invention is to provide an anti-fogging window glass and mirror glass which are hard to be clouded in a rainy day or in winter season and have a durability satisfactory for practical use and a process for preparing these glasses.

Means for solving the Problem

The anti-fogging window glass and mirror glass of the present invention is characterized in that a film of an inorganic oxide such as silica or titania having a certain thickness and fine irregularities on its surface is formed on the surface of glass.

The glass used in the present invention may be the conventional window glass and mirror glass. An inorganic oxide such as Alumina (Al_2O_3) or indium oxide(In_2O_3 doped with Sn) in addition to silica (SiO_2) and titania (TiO_2) is formed on the surface of the glass by the sputtering method. The thickness of the film depends on the kinds of the inorganic oxides, and is preferably in the range of 4,000 - 6,000Å. If the film has a thickness less than 4,000Å, it is poor in durability. Whereas the film having a thickness more than 6,000Å exerts no further effects. By way of example, sputtering is preferably carried out for example at a glass plate temperature of 300℃ or more under the sputtering pressure with argon gas of about 7×10^{-3} Torr, and at a glass plate temperature of 150℃ or more under the sputtering pressure of about 15×10^{-3} Torr.

The film of the inorganic oxide formed on the glass

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plate by the sputtering comprises fine crystal grains. When the surface of the film is chemically etched by an etching agent such as hydrofluoric acid alone or a mixed acid etching agent of hydrofluoric acid and an oxidizing acid such as nitric acid or sulfuric acid or a salt thereof, grain boundary is preferentially etched due to its tendency to be etched more easily than the other parts thus resulting in fine roughness on the surface of the film. For instance, when a 0.15% by weight of hydrofluoric acid solution is used as an etching agent, the glass plate is preferably dipped in the solution for about 30 minutes.

An anti-fogging glass having a transparent appearance and a satisfactory durability is prepared by the treatment described above.

<u>Example</u>

The present invention is now described in more details with reference to the following examples. However, the present invention is not intended to be limited to these examples.

Example 1: Relationship between glass plate temperature and argon gas pressure

A window glass plate was placed in a vacuum bath, which was reduced to a pressure of 10^{-3} Torr before introducing argon as a sputtering gas up to a pressure of 2×10^{-3}, 7×10^{-3}, and 15×10^{-3} Torr, respectively, and SiO_2 was sputtered onto the glass plate to form a film having an average thickness of about 5,000Å. The glass plate was heated to a temperature of 60°, 150° and 300℃, respectively. The glass plate having the film formed thereon was taken out from the vacuum bath, dipped into a 0.15% by weight hydrofluoric acid aqueous solution for 30 minutes to etch the surface of the film. After the etched surface was rinsed with distilled water, the glass plate was dipped into water warmed to 60℃ for a certain time, then rinsed again with distilled water, and dried.

For the respective samples prepared above, the

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contact angle of distilled water and the surface of the glass on which SiO_2 was formed was measured as shown in Fig. 1. In the figure, 1 represents the glass plate, 2 represents SiO_2 sputtered film, 3 represents waterdrop, and 4 represents a contact angle. The result is shown in Table 1.

Table 1: Contact angles (degree) of glass plates prepared under various conditions and water

Argon gas pressure (Torr)	Glass plate temperature (℃)		
	60	150	300
2×10^{-3}	39	28	25
7×10^{-3}	35	22	12
15×10^{-3}	30	16	8

It is found from the result of Table 1 that the glass plate prepared at a higher temperature during the film formation by SiO_2 sputtering and at a higher argon gas pressure gives after etching a lower contact angle with waterdrops and thus wets better. If the contact angle is 16° or less, waterdrops do not keep their shape and are substantially plain, so that they cause no problem of visibility.

An untreated glass plate gives a contact angle with waterdrops of 42°, and a glass plate having SiO_2 film formed thereon prior to etching has a contact angle of 40°. In such glass plates, waterdrops adhered to the surface of the plates act as small lenses thus lowering visibility. Also, when the glass plate treated according to the present invention is used as a window glass of a car, the window glass of the invention having a contact angle of 16° or less is wetted with moisture by the sweat released from persons in the car without clouding because of no formation of small droplets, whereas conventional

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glass plate becomes clouded with moisture.

The anti-fogging phenomenon according to the present invention can be explained as follows.

The film 2 sputtered with SiO_2 has ordinarily a columnar structure almost vertical to the surface of the glass plate 1 as a base plate as shown in Fig. 2. When the film 2 sputtered with SiO_2 having the above described structure is etched with an etching agent such as an HF solution under the certain condition, etching proceeds preferentially at the interface between the columns of the columnar crystal grains, that is the grain boundary, as shown in Fig. 3, and the surface 5 before etching is changed to the post-etched surface 6 thus resulting in caved parts on the etched surface. It is considered that the formation of such fine roughness will make the surface to be wetted with water. In other words, such a phenomenon is the same as that in a ground glass which tends to be wetted with water and is hard to form droplets on its surface.

In addition, different contact angles depending on the sputtering conditions can be explained as follows.

If the temperature of the glass plate is high, the diameter of the columnar crystals, that is the size of the crystal grains is increased, and the roughnesses formed by etching grow larger. Also, the increase of the argon gas pressure will cause the similar phenomenon.

It is believed that when the temperature of the glass plate is low and the argon gas pressure is low, extremely fine columnar crystals are porduced. Thus, after etching, extremely fine roughnesses formed on the surface of the SiO_2 sputtered film 2 exert little effect on the wetting with water.

It is only at the contact angle of 16° or less that the glass plate is judged effective apparently. Suitable conditions for forming SiO_2 sputtered film under the etching condition in this example in order to

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accomplish such a state of the contact angle are at a glass plate temperature of 150℃ or more when the argon gas pressure is 15×10^{-3} Torr or at a glass plate temperature of 300℃ or more when the argon gas pressure is 7×10^{-3} Torr.

Example 2: Relationship between the concentration of hydrofluoric acid and dipping time and the contact angle and cloudiness

SiO_2 was sputtered on a glass plate to form a film having a thickness of 5,000Å at an argon gas pressure of 15×10^{-3} Torr and a glass plate temperature of 300℃. Etching test of the film thus formed was carried out with different concentrations of hydrofluoric acid aqueous solutions and different dipping times to determine the contact angles with droplets of water and to measure cloudiness with a haze meter prescribed in ASTM-D1003-61. Cloudiness was measured at four points. The cloudiness of the conventional window glass is in the range of about 0.15 - 0.1%. The results are shown in Table 2.

Table 2: Contact angle (upper column, degree) and cloudiness (lower column, %) under various etching conditions

Dipping time (min) Concentration (% by weight)	3	10	30	60
2	15 - 3 0.2 - 7	5 - 3 5 - 7	3 7 - 8	3 7 - 8
0.3	19 0.3	8 1.5 - 2.5	5 - 7 - 2	5 - 1 3 - 4
0.15	35 0.15 - 1	17 0.15 - 0.1	8 0.15 - 0.1	8 0.15 - 0.1
0.01	40 0.15 - 1	40 0.15 - 0.1	32 0.15 - 0.1	21 0.15 - 0.1

It is found from the results of Table 2 that when a 2% by weight hydrofluoric acid aqueous solution is used, the sputtered film is etched rapidly but only unevenly to cause slight cloudiness on visual observation after 10 minutes; on dipping for 30 minutes or more, the whole surface is clouded uniformly and the appearance also becomes like a ground glass. In contrast to this, when using a 0.3% by weight hydrofluoric acid aqueous solution, cloudiness is less increased, but when water is sprayed on the surface, stable contact angle is not obtained due to the local formation of water droplets, so that the treated surface is thought to have no uniformity. When the sputtered glass plate is dipped in a 0.15% by weight hydrofluoric acid solution for about 30 minutes - 60 minutes, the treated glass plate has a stable contact angle of 8° and the cloudiness remains stably in the range of

0.15 - 0.1%. In addition, the finish has also an extremely uniform appearance, and when waterdrops are sprayed the surface is wetted uniformly as well. Furthermore, if the concentration of the aqueous hydrofluoric acid is decreased to 0.01% by weight, no etching seems to proceed in the dipping for less than 30 minutes. Also, no expected effect is not obtained even by the dipping for 60 minutes, and thus the etching with such a low acid concentration is inferior in productivity.

Thus, as the etching condition, the dipping in a 0.15% by weight hydrofluoric acid aqueous solution at ordinary temperature for 30 minutes is preferred in view of its property and productivity.

It goes without saying that oxidizing acids or salts thereof such as nitric acid or sulfuric acid in addition to hydrofluoric acid can be also used as the etching solution.

Example 3: Preparation of an anti-fogging window glass with use of a variety of inorganic oxides

As a result of experiment almost similar to those in Examples 1 and 2 replacing SiO_2 with TiO_2, Al_2O_3, or In_2O_3 (doped with Sn), an anti-fogging window glass having a wetting property improved almost to the same level as with SiO_2 was prepared.

Example 4: Relationship between the thickness of the SiO_2 sputtered film and the cloudiness

Anti-fogging window glasses with various thicknesses of SiO_2 film were prepared in the same manner as in Example 1 and subjected to the taper abrasion test according to JIS R3212. The relationships between film thickness and cloudiness before and after etching are shown in Fig. 4. As is apparent from the figure, the cloudiness remains +2% or less of the standard before etching, but the window glasses having a thickness of less than 4,000Å show the cloudiness of 3 - 5% and are inferior in resistance to scuffing. By contrast, the effects are not increased even

if the film thickness of the window glasses is increased. Thus, the window glasses have preferably a film thickness in the range of 4,000 - 6,000Å.

Results of the Invention

As described above, the anti-fogging glass of the present invention has a film of a certain thickness adhered to the surface of the glass, which film comprises an aggregate of crystal grains of inorganic oxide and has fine roughness on the surface, so that the present anti-fogging glass is superior to water wetting property and well suited for the window glass and mirror glass of cars. That is to say, even if water is sprayed on the surface of the present anti-fogging glass, no waterdrops are generated thus significantly improving visibility as compared with untreated glass.

Furthermore, in contrast to the conventional products in which a film of an anti-fogging agent is formed on the surface of glass or a hydrophilic plastic sheet is adhered to the surface of glass, the present product in which a film of a hard inorganic oxide is formed on the surface of glass is superior to durability and thus its anti-fogging effect is still maintained after the working of a wiper for 3,000 hours.

Also, in the process for preparing an anti-fogging glass of the present invention, a film of an inorganic oxide is formed on the surface of a glass by sputtering, so that it can be practiced simply and quickly, a variety of inorganic oxides may be used in combination, and the nature of the film can be easily changed by selecting the conditions. In addition, in order to form roughness on the surface of the film by chemically etching the surface, many acids and various combinations of these acids and salts thereof can be used as an etching agent, and the etching conditions can be selected, so that an anti-fogging glass having desired properties can be easily prepared.

The present invention provides an anti-fogging

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glass which is hard to be clouded in rainy day or in winter season and have a durability satisfactory for practical use. Thus, the application of the product of the present invention to cars improves visibility on driving the car, which enhances the safety as well as the value of the car as an article. In addition, the present invention can be used in a wide range of the other applications such as for ensuring good view at all times and thus exerts various effects as a special glass material.

4. Brief Description of the Drawings

Fig. 1 is a sectional view illustrating the contact angle of the sputtered film and a water droplet adhered to its surface;

Fig. 2 is a view illustrating the structure of the SiO_2 sputtered film formed on the surface of a glass plate;

Fig. 3 is a view illustrating the change of shapes of the surface of the sputtered film before and after chemical etching; and

Fig. 4 is a graph illustrating the relationships between the thickness and cloudiness of the sputtered film before and after chemical etching,

in which

1: glass plate, 2: SiO_2 sputtered film,
3: water droplet, 4: contact angle,
5: surface before etching,
6: surface after etching.

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